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AN EMPIRICAL FORMULA FOR CALCULATING THE DISSOCIATION ENERGY OF ORGANIC MOLECULES

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(Presented by N. N. Semenov, Member of the Academy, September 30, 1952.)

A most important constant, essential for many theoretical and practical calculations, is the energy of dissociation of the different bonds in a molecule. The existing vast amount of experimental data on the question has been set forth in review articles^{1,2}. Nevertheless there does not exist any general theory which would enable us to calculate this quantity.

L. Pauling³ gives a semi-empiric method of calculating the bond dissociation energy, which takes into account the electronegativity of the atoms. But this method, applicable to biatomic molecules with a covalent bond, is not suitable for organic compounds, since it makes no allowance for the mutual influence of the atoms. The weaknesses of Pauling's method were pointed out by A. F. Kapustinski⁴, who suggested a new way of quantitatively calculating the electronegativity of the atoms. More recently, V. V. Voyevodski⁵ has constructed an empirical formula enabling us to calculate the dissociation energy of the C-C and C-H bonds of saturated hydrocarbons.

Since the known empirical relationships are each applicable only to certain specified organic compounds, it seemed worthwhile to find an empirical formula expressing the interconnection between these dissociation energies.

As is well known, the approximate quantitative calculation of the dissociation energy of a monoelectronic covalent bond leads to the relationship:

$$E = k S_A S_B, \quad (1)$$

where E is the dissociation energy of a molecule A-B; k is a coefficient of proportion; S_A and S_B are the strengths of the bonding orbits.* Since this relation is derived for a monoelectronic bond, we cannot mechanically carry it over to a bielectronic bond, as Pauling has done. We may however assume that also in the case of a bielectronic bond the dissociation energy is determined by the strength of the bonding orbits:

$$E_{R_A-R_B} = f(S_A, S_B), \quad (2)$$

* By "strength of a bonding orbit" we mean the maximum amplitude of the wave-function describing the state of the valence-electron of a given atom or radical.

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where $E_{R_A-R_B}$ is the dissociation energy of a molecule R_A-R_B .

Let us consider the dissociation energy of two series of molecules $R-R_A$ and $R-R_B$, where R_A are certain specified radicals and R is variable.

On the basis of equation (2), we find:

$$E_{R-R_A} = f(S, S_A), \quad E_{R-R_B} = f(S, S_B). \quad (3)$$

Since S is a parameter, then between E_{R-R_A} and E_{R-R_B} there must exist a well-defined relationship, a fact which is confirmed by experimental data^{1,2}. Investigating this interrelation between dissociation energies, we found the empirical formula:

$$E_{R_A-R_B} = E_0(1 - e^{-c_A c_B}), \quad (4)$$

where E_0 is an empirical constant depending on the type of bond; c_A and c_B are empirical constants depending on the nature of radicals R_A and R_B .

To convince ourselves of the validity of formula (4), let us compare the dissociation energies of the two series of molecules $R-R_A$ and $R-R_B$:

$$E_{R-R_A} = E_0(1 - e^{-c c_A}), \quad E_{R-R_B} = E_0(1 - e^{-c c_B}). \quad (5)$$

Eliminating c , we get:

$$\ln(1 - \frac{E_{R-R_A}}{E_0}) = \frac{c_A}{c_B} \ln(1 - \frac{E_{R-R_B}}{E_0}). \quad (6)$$

It will be seen from Fig.1 that with proper choice of E_0 a linear relationship between $\ln(1 - \frac{E_{R-R_A}}{E_0})$ and $\ln(1 - \frac{E_{R-R_B}}{E_0})$ is in fact maintained.

At small values of $E_{R_A-R_B}$ formula (4) becomes:

$$E_{R_A-R_B} = E_0 c_A c_B \quad (7)$$

and coincides in form with equation (1), derived from quantitative calculation of the mono-electronic bond.

On the basis of the above, we may take it that the empirical constant c defines the strength of the valence-orbit of a radical.

Using formula (4), we calculated from the experimental data the following values for c and E_0 .

Values of c for various radicals and atoms: cyanogen 1.8, ethinyl 1.77, chlorine 1.67, bromine 1.33, phenyl 1.19, hydrogen 1.17, vinyl 1.16, iodine 1.01, methyl 1.00, ethyl 0.98, n-propyl 0.94, n-butyl 0.90, triiodomethyl 0.88, isopropyl 0.86, acetyl 0.83, formyl 0.82, tribromomethyl 0.82, tertiary butyl 0.82, trichloromethyl 0.73, benzyl 0.66, m-xylyl 0.65, allyl 0.64, α -naphthyl-methyl 0.64, β -naphthyl-methyl 0.64, n-xylyl 0.635, methyl-allyl 0.635, o-xylyl 0.62, triphenyl-methyl 0.31.

Values of E_0 for different types of bond: $E_0^{C-C} = 133$, $E_0^{C-Cl} = 99$, $E_0^{C-Br} = 91$, $E_0^{C-I} = 84$, $E_0^{C-H} = 145$ kcal/mol.

The empirical constants thus found were utilized to calculate some still unknown dissociation energies. The results of the calculation are shown in Tables 1 and 2.

In conclusion, we express our gratitude to Professor G. A. Razuvayev for his valuable guidance in the carrying-out of this work.

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	CH ₄	C ₂ H ₆	n-C ₃ H ₈	n-C ₄ H ₁₀	n-C ₅ H ₁₂	C(CH ₃) ₄	CH=CH ₂	CH ₃ CH=CH ₂	CH ₃ CH=CH-CH ₃	C≡CH	C ₂ H ₂	CH ₃ C≡CH	C≡C-CH ₃	C(CH ₃) ₃	C(CH ₃) ₂	C(CH ₃)	CCl ₄
CH ₄	84.4, 83.9	82.2, 82.9	80.6, 80.9	77.5, 76.7	78	78.7	74.8, 74.3	80.7, 91.1	62.7, 62.6	111.0, 110.1	90.0, 90.9	111.0, 110.1	111.4, 110.7	85.4	71.5	72.6, 74.8	68.1
C ₂ H ₆	81.2, 82.9	80.4, 81.9	79.2, 79.5	76.2, 75.6	78	77.7	72.7, 72.5	87.5, 90.1	61.5, 61.6	108.8, 109.4	88.9, 91.3	108.8, 109.4	109.9	34.8	70.9, 73.5	72.7, 74.1	67.9
n-C ₃ H ₈	80.6, 80.9	79.2, 79.9	77.5, 75.6	74.4, 73.7	75	75.7	71.0, 71.6	86.7, 88.1	59.5, 60.0	107.4, 108	86.7, 88.1	107.4, 108	108.3	33.7	70.9, 71.6	72.5, 72.1	65.9
n-C ₄ H ₁₀	74.5, 76.7	76.2, 75.6	74.4, 73.7	70.5, 69.3	71.7	71.6	66.0, 67.1	83.7, 83.9	54.5, 55.1	103.0, 103.9	83.7, 85.3	103.0, 103.9	104.3	31.0	67.1	73.7, 68.8	61.1
n-C ₅ H ₁₂	78	77.7	78	75.7	74.4, 74.0	69.2, 69.1	66.3, 66.1	86.3, 86.1	55.5, 57.8	106.0	87.7, 87.3	106.0	107.4	32.8	69.1	70.0	63.1
C(CH ₃) ₄	74.8, 74.3	72.7, 72.5	70.1, 71.6	65.6, 65.1	69.2	69.1	65.6, 64.9	70.8, 81.7	54.5	101.7	78.7, 82.6	101.7	97.6	29.9	64.9	65.4	60.9
CH=CH ₂	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	80.7, 91.1	40.1	82.1, 81.7	82.1, 81.7	75.8
CH ₃ CH=CH ₂	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	61.5, 62.6	28.9	51.1, 54.0	54.6	44.3
C≡CH	111.0, 110.1	109.2, 109.7	108.8, 108.3	103.0, 103.9	106.0	106.0	106.0	106.0	106.0	106.0	106.0	106.0	106.0	56.1	101.7	102.2	96.6
C ₂ H ₄	90.0, 92.9	91.2, 91.7	88.9, 89.4	83.7, 85.3	87.7	87.7	87.7	87.7	87.7	87.7	87.7	87.7	87.7	41.0	80.6, 82.6	83.3	73.9
CH ₃ C≡CH	62.4, 64.0	60.8, 63.1	59.4, 61.2	54.5, 57.0	57.5, 59.8	55.5	55.5	55.5	55.5	55.5	55.5	55.5	55.5	24.5	55.5	63.7	50.7
C(CH ₃) ₃	35.4	31.8	33.7	31.0	32.8	29.9	29.9	40.1	23.9	56.1	41.0	56.1	56.6	27.1	29.9	30.1	27.1
C≡O	71.5	70.5	70.5	67.1	69.1	64.9	64.9	82.1, 81.7	51.1, 54.0	101.7	80.6, 82.6	101.7	97.6	29.1	64.9	64.9	60.9
C≡O	71.5	70.5	70.5	67.1	69.1	64.9	64.9	82.1, 81.7	51.1, 54.0	101.7	80.6, 82.6	101.7	97.6	29.1	64.9	64.9	60.9
CN	111.4, 110.7	110.7	110.7	104.3	106.9	97.6	97.6	114.1, 116.0	93.7, 90.7	127.1	122.1, 116.5	127.1	127.2	56.6	97.6	103.9	97.1
CCl ₄	66.7	67.9	66.8	6.1	63.9	60.0	60.0	75.9	49.3	96.6	75.9	96.6	97.1	27.1	60.0	60.2	57.9

* The figure at the right in each cell is the calculated value; at the left, the experimental values (above, data from reference 1; below, data from reference 2).

Table 2
Dissociation energies of organic molecules in kcal/mole.*
C-H, C-Cl, C-Br, C-I bonds.

	H	Cl	Br	I
CH ₄	101,1 100,0	80,7 80,5	67,4 ~68	53,1 ~54, < 58
C ₂ H ₆	~99 98,5	79, 79,8	64,6 66,5	52 ~52, ~51 52,4
n-C ₃ H ₈	~95 96,7	77,42 78,5	64,9	~50 51,1
n-C ₄ H ₁₀	90,8 89,2	76 75,4	62,1	~46 48,5
n-C ₅ H ₁₂	~94 94,3	77,6	63,6	~49 49,9
C(CH ₃) ₄	86? 89,2	74,7 73,9	60,8 60,4	45? 47,0
CH=CH ₂	922 102? 107,5	84,9 84,6	71,6	~55 57,6
CH ₂ CH=CH ₂	~77; ~78 76,4	59,32 64,9	48±5 52,1	34,4 39? 35-37 39,7
C≡CH	<121 126,5	93,9	82,5	69,6
C ₆ H ₆	102? 108,4	86,3? 85,4	72,5	~57? 58,5
CH ₂ C ₆ H ₅	77,5±1,5 77,9	66,1	48,5? 50±2	36,5 44? ~39 40,6
C $\begin{smallmatrix} \text{O} \\ \parallel \\ \text{H} \end{smallmatrix}$	89,2	73,9	60,4	47,0
C $\begin{smallmatrix} \text{O} \\ \parallel \\ \text{CH}_3 \end{smallmatrix}$	90,0	76,7 74,1	62 67	46,0 61,0 47,4 51,0?
CN	121,1 127,1	94,8 94,2	82,6	71,2 70,1

* The figure at the right in each cell is the calculated value; at the left, the experimental values (above, data from reference 1; below, data from reference 2).

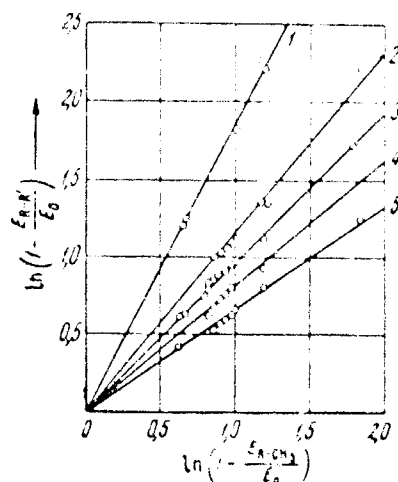


Fig. 1. Interrelation of dissociation energies of certain organic molecules.

1. R'≡CN
2. CH=CH₂
3. CH₂CH₃
4. C(CH₃)₃
5. CH₂C₆H₅